(12) UK Patent Application (19) GB (11) 2 163 790 A

(43) Application published 5 Mar 1986

(21) Application No 8421761

(22) Date of filing 28 Aug 1984

(51) INT CL[4]
E21B 43/27

(52) Domestic classification
E1F PD

(56) Documents cited
GB A 2110744 GB 1562308 EP A 0007012

(58) Field of search
E1F

(71) Applicants
The Dow Chemical Company (USA-Delaware)
2030 Dow Centre, Abbot Road, Midland, Michigan 48640,
United States of America

(72) Inventor
Warren L. Nehmer

(74) Agent and/or Address for Service
W. H. Beck Greener & Co., 7 Stone Buildings, Lincoln's Inn,
London WC2A 3SZ

(54) Methods for acidizing subterranean formations and gelled acid compositions

(57) Gellable and gelled acid compositions comprise an aqueous acid, and a water-soluble polymer comprising, for example, acrylamide and methacryloylethyl trimethyl ammonium chloride. Optionally, the composition includes a reducing agent such as erythorbic acid. The gelled acids are useful in acidizing subterranean formations and such gels are stable to degradation by heat and do not yield insoluble residues when used in the presence of ferric ions.

GB 2 163 790 A

SPECIFICATION

Methods for acidizing subterranean formati ns and gelled acid compositions

This invention pertains to improved compositions and methods for acid treating or acidizing of subterranean formations in order to stimulate the production of formation fluids.

Acid treating or acidizing of porous subterranean formations penetrated by a well bore has been widely employed for increasing the production of fluids, such as crude oil, natural gas, etc., from said formations. The usual technique of acidizing a formation comprises introducing a nonoxidizing acid into the well under sufficient pressure to force the acid out into the formation where it reacts with the acid-soluble components of the formation. The technique is applied to formations of high acid solubility, such as limestone, dolomite, etc. and is also applied to other types of formations containing streaks or striations of acid-soluble components such as sandstone containing carbonate striations.

During acid treatments, passageways in the formation for fluid flow are created or enlarged thus stimulating the production of fluids from the formation. This action of the acid on the formation is often called etching. There are essentially two well-known types of acid treatments used in the field, and these include matrix acidizing and fracturing acidizing. Both types of treatments utilize acid compositions as pumpable fluids. In matrix or acidizing operations, wherein the acid is injected into the formation at a pressure or rate sufficient to force the fluid into the formation eut insufficient to hydraulically fracture the formation. In fracture acidizing operations, the acid composition, which is usually in the form of a viscous gel, is used as a fracturing fluid which is pumped through the well bore into the formation at a sufficient rate and pressure to overcome the overburden pressure and thus fracture the formations.

One of the problems commonly encountered in acidizing operations is insufficient penetration of the formation by the acid. Good penetration is necessary in order to realize maximum benefits from the acidizing operation. Too often the acid spends essentially completely in the area immediately adjacent and surrounding the well bore. The severity of this problem increases with well depth and with increasing temperatures which enhance the reaction of the acid with the formation.

Poor penetration can also be caused and/or aggravated by fluid loss to the more porous zones of the formation or "thief zones." Poor penetration can also b caused and/or aggravated by leak-off at the fracture faces in fracture-acidizing operations. Fluid loss or leak-off can fr quently worsen the situation by leaving the tight (low perm ability) zones of the formation unchanged while opening up the already high permeability z n s. On solution which has been proposed for th above discussed problem is to incorporate various thickening or gelling agents into the acid solutions. Such agents thicken the acid solution and increase th visc sity ther of. It has b en disclosed that polymer-thickened acid solutions hav improv d fluid l ss properties. For example, see U.S. Patent No. 3,415,319 issued to B. L. Gibson; and U.S. Patent No. 3,434,971 issued to B. L. Atkins. It has also been disclosed that the reaction rate of said polymer-thickened acid solutions with the acid-soluble portion of the formation is lessened or retarded. See, for example, U.S. Patent No. 3,749,169 issued to J. F. Tate; U.S. Patent No. 3,236,305 issued to C. F. Parks,; U.S. Patent No. 3,252,904 issued to N. F. Carpenter; and U.S. Patent Nos. 4,055,502; 4,103,742 and 4,191,657 issued to Swanson. It has been disclosed that foams, including foamed acids, have improved fluid loss properties. For example, U.S. Patent No. 3,937,283 issued to Blaner and U.S. Patent No. 4,235,734 issued to Schernkel disclose foamed acid systems which can be used for foam fracturing. However, such foams have stability problems.

Higher viscosity fluids have other advantageous fracture-acidizing operations in that the more viscous acidic solutions produce wider and longer fractures. More viscous acid solutions are also more effective in carrying propping agents into the formation when propping agents are used.

Another problem encountered in acidizing operations, particularly when employing acidizing compositions having thickening or viscosifying agents incorporated therein, is stability to heat. By "stability to heat" is meant the retention of the increased or greater viscosity properties under the conditions of use. Such compositions to be satisfactory should be sufficiently stable to resist thermal degradation in the presence of acid for a period of time sufficient for the gelled acid to accomplish the intended purpose, e.g., good penetration and significant etching of the formation. The degree of stability required in any particular operation will vary depending upon the type of formation being treated, the temperature of the formation, the well depth, acid concentration, pump rates, shear rates, etc. For example, in acidizing a low permeability formation, one proceeds more slowly (i.e., at lower iump rates and lower pressures) than with a more permeable formation, other factors being the same, because a longer residence time will be required to obtain a significant amount of etching.

The temperature of the formation usually has a pronounced effect on the stability of the acidizing compositions and, generally speaking, is one of the most important operating variables when considering stability. Increased formation temperatures usually have at least two undesirable effects. One effect is polymer degradation which results in a decrease in viscosity. Another effect is increased rate of reaction of the acid with the formation. Thus, some compositions which would be satisfactory in a low temperatur formation such as in the Hugot n fi ld in the Anadarko basin might n t be satisfactory in formati ns encountered in d eper wells as in some W st Texas fields. An th r pr blem which is som times enc unter d when using thickened compositions in treating formations involves flow-back or removal of the treating composition after the operation is complet d.

In ordinary acidizing operations using unthickened acids th re is usually no problem in removing the spent acid because it is essentially water. However,

some r sidues from the spent thickened or visc us acid solutions are difficult to remove from the pores of the formation of the fracture after the operation is complete. Som times th polymeric gelling agent precipitates from the spent acid and forms a clogging residue in the pores of the formation, or in the fracture. This can inhibit the production of fluids from the formation and can require costly cleanup operations.

During such acid treatments, the treatment acid often dissolves iron scale in pipes and iron-containing minerals in the formation. The dissIved iron normally remains in solution until the acid is spent. Upon spending, ferric hydroxide begins to precipitate and plug the formation. Complete precipitation of ferric hydroxide is reached at a pH of about 3.2. Ferrous hydroxide, being more soluble, does not begin to precipitate until a pH of approximately 7.7 and is not generally a problem.

The deleterious effects of ferric hydroxide in wells was recognized by Grebe in U.S. Patent No. 2,175,081 as early as 1937 where a strong acid containing sulfurous acid is disclosed as a means of countering the precipitation problem. Numerous other procedures have been proposed for avoiding the ferric hydroxide problem. For example, U.S. Patent No. 2,175,095 suggests including within the acidizing fluid a material such as lactic acid, ammonium acetate, glycine, glycolic acid, citric acid, or the like, which is capable of preventing the precipitatin of iron or aluminium hydrates at normal precipitation pH values. U.S. Patent No. 2,335,689 suggests adding an iron sequestering agent, such as a polyhydric phenol, within the injected acids. U.S. Patent No. 3,142,335 suggests the use of a sequestering agent containing a mixture of ingredients that function as a pH buffer, such as citric acid or a citrate salt mixed with acetic or formic acids or their salts. U.S. Patent No. 3,150,081 suggests using mixtures of hydroxyacetic and citric acids, which mixtures are alleged to be more effective than the use of either acid alone.

The most common sequestering agents in commercial practice are citric acid, ethylenediamine -tetraacetic acid (EDTA), nitrolotriacetic acid (NTA), acetic acid, lactic acid, and citric acid/acetic mixtures. Data on these sequestering agents is found in the paper by Smith et al., Paper No. SPE 2358, Society of Petroleum Engineers of AIME, (presented November 7-8, 1968).

The problem with most iron sequestering agents is that they are not particularly effective at temperatures beyond about 125°-150°F (51.7°-65.6°C). Only NTA, citric acid and EDTA have shown any effectiveness at higher temperatures. Of these, EDTA is the only practical sequestering agent because citric acid tends to form insoluble citrates during the course of the well treatment. Such citrates can block the well production almost as effectiv ly as the ferric hydroxid .

The presence of ferric ions in the treatment acid s lution is known to cause other s rious problems as well. For example, U.S. Patent No. 4,096,914 teaches that ferric ion reacts with asphaltenic oil to form ins luble ironasphalt n comp unds. Thes compounds are insoluble precipitates which likewise plug the formation channels and inhibit production of the desired fluid. The patent teaches that the problem can be solved by incorporating salicylic acid into the treatm nt acid.

Ferric ion corrosion can also be a problem. Two m les of feric ion react with base metal to form three mol s f ferrous ion. Almost any oxidizing sourc readily converts the ferrous ions to ferric ions, and a vicious circle results. Additives used to control problems associated with ferric ions in treatment of wells have been called "iron stabilizers" or "iron control agents" by practitioners in the field.

Another problem associated with the presence of ferric ions in a polymerically thickened acid composition involves the precipitation of the polymer. That is, a precipitate forms which is believed to contain iron in a chemically combined form (i.e., such as a metal ion crosslinker) with the polymer. The precipitate is usually in the form of a gummy, insoluble mass that is very difficult, if not impossible, to resolubilize under the conditions of use for acid treatment fluids.

In view of the deficiencies of the prior art, it would be highly desirable to provide a gellable or gelled acid composition for use in acidic well treatments and a method of using same, which composition is viscous, stable and generally free of insoluble precipitates during use.

In one aspect, the present invention is a gellable or gelled acid composition which comprises an aqueous acid thickened with a functionally effective amount of a water-soluble polymer comprising (1) a nonionic water-soluble ethylenically unsaturated monomer and (2) a water-soluble ethylenically unsaturated monomer containing a cationic moiety, wherein said polymer provides increased viscosity to the composition during acid treatment of porous subterranean formations; which amount of polymer is sufficient to cause gelation and to form a gelled acid formulation sufficiently stable to degradation by heat of said formations.

In another aspect, the present invention is a method for acid treating a porous subterranean formation susceptible to attack by an acid which formation is penetrated by a wellbore; which method comprises injecting into said formation via said wellbore a gellable or gelled acid composition comprising an aqueous acid in an amount capable, and sufficient for, reacting with a significant amount of the acid-soluble components of said formation, and a water-thickening amount of water-soluble polymer comprising (1) a nonionic water-soluble ethylenically saturated monomer and (2) a water-soluble ethylenically unsaturates monomer containing a cationic moiety; said polymer and said acid in the amounts used, being sufficiently compatible with each other in an aqueous dispersion thereof permit said gelation and thus form said composition having sufficient stability to degradation by the heat of said formation to permit good p netration of said composition into said formation; and maintaining said composition in said formation in contact therewith for a period of tim sufficient usually for the acid in said composition to react significantly with the acid-soluble comp nents of said formation and stimulate the production of fluids therefrom.

The process of this invention yields a means of providing increased production of oil or gas. The novel acid c mposition can be used for fracture

acidizing. The polymer of this inv ntion provides an improved means for reducing the rate at which fluid is lost into th subterranean formation. The acid is also used for matrix acidizing. The polymer of this invention provides a slow rate of reaction of acid within the subterranean formation to increase penetration of said acid into the formation. In either case, the reducing agent prevents problems associated with insoluble residues caused by ferric ions.

Ethylenically unsaturated, water-soluble monomers suitable for use in the this invention are those which are sufficiently water-soluble when dissolved in water and which readily undergo polymerization to form polymers which are at least inherently water-dispersible and preferably water-soluble. By "inherently water-dispersible" is meant that the polymer when contacted with an aqueous medium, will disperse therein without the aid of surfactant to form a colloidal dispersion of polymer in the aqueous medium.

Exemplary nonionic monomers suitably employed in the practice of this invention are those ethylenically unsaturated monomers that are sufficiently water-soluble to form at least a 5 weight percent solution when dissolved in water and readily undergo addition polymerization to form polymers that are water-soluble. Examples of such nonionic monomers include ethylenically unsaturated carboxamides such as acrylamide, methacrylamide and fumaramide; their water-soluble N-substituted nonionic derivatives such as the N-methylol derivatives of acrylamide and methacrylamide as well as the N-methyl and N,N-dimethyl derivatives of acrylamide and methacrylamide; hydroxyalkyl esters of unsaturated carboxylic acids such as 2-hydroxyethl acrylate and 2-hydroxypropyl acrylate; and the like. Of the foregoing nonionic monomers, the ethylenically unsaturated carboxamides are preferred, with acrylamide being especially preferred.

Cationic polymers suitably employed in the practice of this invention are copolymers of the aforementioned nonionic monomers and ethylenically unsaturated monomers containing moieties such as the acryloylalkyl trialkyl ammonium salts (i.e., acryloylethyl trimethyl ammonium chloride); the methacryloylalkyl trialkyl ammonium salts (i.e., methacryloylethyl trimethyl ammonium chloride); the acrylamido- and methacrylamido-alkyl trialkyl ammonium salts (i.e., acrylamidopropyl trimethyl ammonium chloride and methacrylamidopropyl trimethyl ammonium chloride); and the like. Of the monomers containing cationic moieties, methacryloylethyl trimethyl ammonium chloride is most preferred.

Polymers useful herein are cationic polymers. The cationic sites can be supplied from copolymerization f a cati nic m nomer or by a subs quent quaternization reaction between an alkylating reactant and some moiety or a (co) polymer. Polymers are prepared by copolymerizing said nonionic ethylenically unsaturated monomers with cationic ethylenically unsaturates monomers using techniques known in the art for preparing water-soluble polymers. For example, poly erization can be carried out in aqueous medium in the presence of a small but effective amount of a water-soluble oxyg n-containing catalyst at a temperature of from 80°F to 190°F (26.7°C to 87.8°C). The resulting polymer is recovered from the aqueous medium, as by drum drying or precipitation, and can b subsequently ground to the desired particle size. The particle size should be fine enough to facilitate the dispersion of the polymer in water. Polymers are most preferably prepared using polymerization techniques described in U.S. Patent No. 3,284,393 and U.S. Patent RE 28,474. Alternatively, the polymers can be prepared by reacting various known alkylating reagents with suitable copolymers so as to form cationic sites on the polymer.

Molecular weights of the polymers of this invention can vary. Molecular weights typically range from 100,000 to 25 million. Most preferably molecular weights range from 1 million to 5 million.

It is believed that the cationic moieties present in the polymer provide heat stability and help prevent the formation of an insoluble residue during the acid treatment of subterranean formations. The nonionic moieties in the polymer are believed to provide thickening capability.

The polymers of this invention exhibit good heat stability at temperatures up to 300°F (149°C) and to substantially prevent the formation of insoluble residues during acid fracturing. The polymer is used in amounts sufficient to provide good thickening (i.e., viscosity) to the composition. The polymers of this invention typically comprise from 1 to 99, preferably from 1 to 50, most preferably 5 to 40, mole percent cationic monomer which is preferably methacryloylethyl trimethyl ammonium c loride, and from 1 to 99, preferably from 50 to 99, most preferably from 60 to 95, mole percent nonionic monomer which is preferably acrylamide. The polymers of this invention can undergo an amount of hydrolysis without deleteriously affecting the properties of the polymer for use herein. For example, 0 to 50, preferably 0 to 5, mole percent of the nonionic monomer can be hydrolyzed.

The composition of this invention comprises from 0.4 to 35, preferably from 3 to 28 weight percent acid, from 0.01 to 5, preferably from 0.1 to 2 percent polymer, and from 60 to 99.6 percent, preferably from 70 to 96.9 weight percent water based on the total weight of the composition. In addition it may be desirable to add corrosion inhibitors, sequestering agents, demulsifying agents, surfactants, friction reducers, and the like, which are commonly added to such types of formulations. Further, the acid compositions can be foamed by including the appropriate foaming agent and a gas, such as nitrogen.

Iron control agents which can also be employed in the composition of the invention are the chelating agents. Any member(s) of the known classes of compounds can be used herein so long as the chosen member(s) is compatibl with th g lled acidic composition, i.e., the chosen member(s) is soluble or dispersibl in the acidic comp sition and does not pr vent formation of th gelled acidic compositi n or caus premature breaking of the gel. Examples of the class of chelating agents for ferric ion includ the polyalkylenepolyaminepoly - carboxylic acids (e.g., N,N',6,N'6 - ethylenediaminetetraacetic acid (EDTA), N - 2 - hydroxyethyl - N,N'6,N'6 -ethylen diamine - triacetic acid (HEDTA) and the liue) and soluble salts

thereof (e.g., tetrasodium EDTA, amm nium salts of EDTA or HEDTA), the hydroxy-containing organic acids (e.g., citric acid, lactic acid and the like) and other such compounds. The chelating agent is included in th g lled acidic composition in a functionally effective amount, i.e., the amount sufficient to prevent or substantially prevent the formation of an onsoluble residue when the gelled acidic composition is contacted, for example, with calcium carbonate in the presence of dissolved iron. Typically, one mole of chelating agent is employed to control each mole of ferric ion.

Small amounts of polymer will usually produce liquid mobile gels which can be readily pumped. Larger amounts of polymer will usually produce thicker, more viscous, somewhat elastic gels. Gels having a viscosity "too thick to measure" by conventional methods can still be used in the practice of the invention. Thus, there is really no fixed upper limit on the amount of polymer which can be used so long as the gelled acid composition can be pumped in accordance with the methods of the invention.

Acids useful in the practice of this invention can include, for example, inorganic acids such as hydrochloric acid, phosphoric acid, nitric acid, hydrofluoric acid and a mixture of hydrochloric acid and hydrofluoric acid; C_1-C_4 organic acids such as formic acid, acetic acid, propionic acid, butyric acid and mixtures thereof and combinations of inorganic and organic acids. The nonoxidizing acids are preferred. The concentration or strength of the acid can vary depending upon the type of acid, the type of formation being treated and the results desired in the particular treating operation. Most preferably, the acid used in the practice of this invention is an inorganic acid such as hydrochloric acid.

The gelled acid composition of the present invention can be prepared on the surface in a suitable tank equipped with a suitable means for mixing and then pumped down into the well and into the formation employing conventional equipment for pumping acid compositions. Most preferably, the polymer is mixed with the acid at temperatures of from 60° to 90°F (15.6° to 32.2°C). Viscosity development is quite rapid and complete viscosity development occurs in 60 to 90 minutes. It is within the scope of this invention to precede the injection of the gelled acid composition with a pad fluid or preflush such as gelled water, aqueous potassium chloride, aqueous ammonium chloride, etc. Such fluids serve to cool the well tubing and formation and extend the useful operating temperature range of said formulations. The volume of the pad fluid so injected can be any suitable volume sufficient to significantly decrease the temperature of the formation being treated and can vary depending upon th characteristics of the formation. Typically, the formulations of this invention are employed at t mp ratur s up to ab ut 300°F (149°C), depending upon conditions of employment and the amount of polymer which is used.

The g lled acid comp sitions of the inventi n can be prepared on the surface in a suitable tank equipped with suitable mixing means, and then pumped down the well and into the formati n mploying conv nti nal equipment for pumping acidic compositions. However, it is within the scope of the invention to prepare said formulations while they ar being pumped d wn the well. This technique is sometimes referred to as "on the fly." For example, a s lution of the p lymer in water can be prepared in a tank adjacent the well head. Pumping of this solution through a conduit to the well head can be started. Then, downstream from the tank, a suitable connection can be provided for introducing the acid into said conduit. A foamed acid can be generated by subsequently introducing a gas such as nitrogen into the flowing stream of acid composition. As will be understood by those skilled in the art, the rate of introduction of said components into said conduit will depend upon the pumping rate of the polymer solution through said conduit. Any of the above-mentioned orders of addition can be employed in said "on the fly" technique. Mixing devices can be provided in said conduit, if desired.

For fracture acidizing treatments the compositions of this invention are injected into a borehole at a sufficient rate and pressure to initiate and propagate a crack or fracture in the formation. Sand, bauxite or other proppant material may be included in the treating to prevent the fracture from closing. In a matrix acidizing operation the treating fluid is injected into the borehole at a rate and pressure sufficient to force the acid out into the formation but insufficient to cause fracturing of the formation.

The following examples will serve to further illustrate the invention but should not be considered as limiting the scope thereof. Unless otherwise noted all parts and percentages are by weight.

Example 1

The present composition is prepared as follows. A volume of concentrated hydrochloric acid is mixed with sufficient water to yield an acid concentration of 28 percent. To 300 ml of this solution is added 6 ml of an emulsion comprising a random copolymer containing 7.5 mole percent methacryloylethyltrimethyl ammonium chloride and 92.5 mole percent acrylamide monomer and having a molecular weight greater than 3 million. The emulsion is about 28 percent polymer solids, such that the polymer is added at a ratio of 0.55 g/100 ml of acid solution. To this solution is also added 0.6 ml/100 ml of acid solution of a corrosion inhibitor. The viscosity of the composition is 65 cps (0.065 Pa·s) as determined at 75°C and a shear rate of 170 sec^{-1} using a Fann 35 viscometer.

Tests for residue formation is determined by placing the acid composition so prepared in a water bath at a temperature of about 185°F (85°C) for a minimum of 2 hours. Marble chips are slowly added to the composition to spend the acid. Addition of the marble chips is continu d until bubble formation c ases. No r sidu formation is obs rv d in the reacted compositi n even after 3 days of heating said compositi n in a water bath at 185°F (85°C).

Example 2

Viscosities of various thick ned acid compositi ns are measured at various temperatures. Th copolymer as is described in Example 1 is added to each aqueous acid sample as an emulsion and in amounts described in Example 1. The various thickened acid

compositions ar plac d into a wat r bath and the visc sity f ach sampl is measured at a shear rate of 170 sec^{-1} using a Fann 35 viscometer. Viscosities of th various samples at various temperatures are presented in Table I.

TABLE I

Temp. (°C)	Viscosity Pa·s at 170 sec^{-1} 15% HCl	20% HCl	28% HCl
15.6	0.063	0.063	0.069
23.9	0.058	0.0576	0.0654
37.8	0.0486	0.048	0.055
51.7	0.0438	0.043	0.0504
65.6	0.040	0.0396	0.0456
79.4	0.036	0.0354	0.0408
85.0	0.0318	0.0318	0.037
93.3	0.0294	0.027	0.0324

The data in Table I indicates good thickening ability of the copolymer in an acid solution, even at temperatures as high as 93.3°C.

Example 3

Sufficient ferric chloride is added to a 28 percent aqueous hydrochloric acid solution to give a ferric ion concentration of 3,000 ppm. This acid solution is then gelled by blending in a water-in-oil emulsion having approximately 28 weight percent of a cationic polymer (92.5 mole percent acrylamide and 7.5 mole percent methacryloylethyltrimethyl ammonium chloride) in amounts of 0.55 grams (g) of cationic polymer per 100 milliliters (ml) of hydrochloric acid solution. Sodium erythorbate is then blended into the gelled acid in an amount of 0.24 g per 100 ml of gelled acid. Marble chips are subsequently added in an amount more than sufficient to spend the acid, and the mixture is heated at 150°F (65.6°C) until the evolution of carbon dioxide ceases. Visual examination of the resulting spent acid shows no polymer precipitate or residue.

In duplicate experiment experiment, using the same gelled acid formulation except that no sodium erythorbate is included, substantial polymer precipitate or residue is observed in the spent gelled acid.

In a duplicate experiment using the same gelled acid formulation except that no sodium erythorbate and no ferric chloride are included, no polymer precipitate or residue is observed in the spent gelled acid.

This series of experiments shows: (1) that the cationic polymer is an effective gelling agent for 28 percent hydrochloric acid, and (2) that the combination of cationic polymer and reducing agent effectively gels 28 percent hydrochloric acid and effectively prevents precipitatin of the polymer spent acid even when substantial am unts of dissolved f rric ion is present.

Example 4

A fracture acidizing treatment is p rformed on a well in th Georgetown formati n in Texas having a bottom hole static temperature of 251°F (121.7°C). The treatment consists of sequentially injecting at fracturing rates and pressures: (a) 25,000 gallons (94.6 m^3) f water lightly gell d with hydroxypropylaguar as a pad fluid, (b) 20,000 gallons (75.7 m^3) of gelled 28 percent hydrochloric acid, and (c) 40,000 gallons (151.4 m^3) f water lightly gelled with hydroxypropylguar as a flush. The well is shut-in for a period of time to let the acid spend, and then slowly brought back onto production. Initial data show the treatment to be successful. The treatment fluids are returned without any observable polymer precipitate or residue in the spent fluids.

The gelled acid contains 20 gallons (0.0757 m^3) of a water-in-oil emulsion of a cationic polymer (per Example 1 above) and 10 pounds of sodium erythorbate per 1000 gallons (3.785 m^3) of 28 percent inhibited hydrochloric acid. The gelled acid has a viscosity of at least 30 to 40 centipoises (0.03 to 0.04 Pa·s) at temperatures of from 90° to 100°F (32.2° to 37.8°C).

CLAIMS

1. A gellable or gelled acid composition which comprises an aqueous acid thickened with a water-soluble polymer of (1) a nonionic water-soluble ethylenically unsaturated monomer and (2) a water-soluble ethylenically unsaturated monomer containing a cationic moiety, wherein the polymer is such as to provide increased viscosity to the composition during acid treatment of porous subterranean formations, and wherein the amount of polymer employed is sufficient to cause gellation and to form a gelled acid composition which is stable to degradation by heat.

2. A composition as claimed in Claim 1, wherein the acid is hydrochloric acid.

3. A composition as claimed in Claim 1 or Claim 2, wherein the polymer comprises from 50 to 99 mole percent acrylamide, and from 1 to 50 percent methacryloylethyltrimethyl ammoniun chloride.

4. A composition as claimed in any one of the preceding claims which comprises from 3 to 28 weight percent acid, from 0.1 to 2 weight percent polymer and from 70 to 96.9 weight percent polymer and from 70 to 96.9 weight percent water.

5. A composition as claimed in any one of the preceding claims, which also includes a chelating agent.

6. A composition as claimed in any one of the preceding claims including at least one reducing agent in an amount sufficient to prevent or to substantially prevent the formation of an insoluble residue as the gelled acid reacts with the acid-soluble components of a subterranean formation in the presence of dissolved ferric ion.

7. A composition as claimed in Claim 6, wherein the reducing agent is ascorbic acid, erythorbic acid, and/or a salt thereof.

8. A composition as claimed in Claim 6 or Claim 7, wherein the said reducing agent is employed in a concentrati n of at l ast 0.6 g/100 ml of acid composition for each 1000 ppm of ferric ion present.

9. A gelled or gellable acid composition substantially as hereinbefor d scribed in any of the foregoing specific Examples.

10. A method for acid treating a porous subterranean formati n susceptible to attack by an acid which formation is penetrated by a wellb re; which method compris s injecting into said formation via said

wellbor a gellable or gelled acid c mposition as claimed in any one of Claims 1 to 8, the composition having sufficient stability to degradation by the heat of the said formation t permit good p netration of the compositions in the formation; and maintaining the composition in the formation in contact therewith for a period of time sufficient for the acid in the composition to react significantly with the acid susceptible components of the formation.

11. A method as claimed in Claim 10, wherein the composition in use includes ferric ions, and a reducing agent, the reducing agent being employed in an amount of at least 0.6 g/100 ml of the composition, for each 1000 ppm of ferric ion present.

12. A method of treating a subterranean formation substantially as hereinbefore described in Example 4.

Printed in the United Kingdom for Her Majesty's Stationery Office, 8818935, 3/86 18996. Published at the Patent Office, 25 Southampton Buildings, London WC2A 1AY, from which copies may be obtained.